

KINETIC MODEL FOR COAL PYROLYSIS OPTIMIZATION

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1. Introduction

Most coal conversion processes, liquefaction as well as gasification, are conducted at elevated temperatures ($> 400.^\circ\text{C}$). At these temperatures the coal decomposes to yield volatiles (tars and gases) and a solid residue (char). If this is done in an inert atmosphere then the coal will only pyrolyse. However, if there is a reacting ambient atmosphere (e.g. hydrogen or steam), in addition to the pyrolysis, gasification of the char and reactions of the volatile matter with the reacting gas will occur. Before we can model the complex situation with a reacting ambient gas, a better understanding of the pyrolysis of coal in an inert atmosphere must be obtained .

Most of the conversion processes that have been or are being developed at present are based only on experimental results obtained in bench scale experiments or in so-called process development units. Since these experiments are time and money consuming, the whole range of process parameters can not always be covered. Hence it is never certain whether the optimum conditions for a specific process have been found, after a limited series of experiments. Here a theoretical modeling technique would be a much more efficient way of optimizing the process. Any theoretical model for a pyrolytic coal conversion process would be based on a) a kinetic model for coal pyrolysis and b) a mathematical model of the flow reactor.

The purpose of this study is to establish a chemical kinetic model which later will be coupled with fluid-mechanical models for several flow reactors. This kinetic model should be applicable over a wide range of operating conditions (e.g. temperature, heating rate) in order that the optimization of a new process not be limited by the applicability of the kinetic scheme. The kinetic scheme should be able to distinguish between condensible tars and non-condensing gases, to allow the optimization of either liquefaction or gasification processes.

Our chemical kinetic model will be based on experimental results that have been reported in the literature. However, a number of simplifications will be introduced because the available data do not

always contain the specific information that is necessary to obtain kinetic values for our scheme. Since most of the published experimental results are for high volatile A bituminous coals, we limited our attention to such hvAb coals for the first approach.

Before we can postulate a kinetic scheme for coal pyrolysis we have to define the characteristic parameters of coal pyrolysis and specify the range in which these parameters might vary.

The pyrolysis of coal leads to two general products: a) the volatile matter which may be divided into pitch, tar, light oil, gases and carbonization water, and b) solid residue comprising coke or char. Pitch, tar and light oils are often simply lumped together and called tars. The carbonization water includes the ammonia. The product gases account for everything that is gaseous at standard temperature and pressure, such as hydrocarbons (saturated and unsaturated), hydrogen, and oxides of carbon. Pitch is a solid at standard temperature and pressure, but since it leaves the reactor as volatile matter, it is lumped in with the tars.

The variables and their typical range to be considered in the modeling of a coal pyrolysis process for a given coal include:

- A) final process temperature (400 C up to above 1000 C)
- B) the heating rate or temperature history of the coal (10^{-4} C/sec up to 10^5 C/sec, corresponding to heat-up times ranging from several months to as short as ten milliseconds.)
- C) coal particle size ($10\text{ }\mu\text{m}$ up to several mm)
- D) pressure in the reactor (1 atm to 50 atm)
- E) residence time of the coal and the volatile matter in the reactor, which is dependent on the type of the reactor (e.g. fixed bed counter-flow, entrained-flow, etc.) and the reactor size.

The residence time of the products in the reactor is determined by the bed depth and the flow rate of sweep gas through the reactor. The temperature history of each coal particle is determined by the temperature of the gas and the pressure in the reactor, as well as by the coal particle size. However, for our parametric studies, we will specify a certain heating rate as an independent parameter, and then the gas temperature and the coal particle size needed to best accomplish this temperature history can be selected separately.

2. Review of Previous Relevant Work

A General References

The pyrolysis of coal has received substantial attention for decades but until about 15 years ago most of the work was concerned

with coal carbonization and coke production, i.e. coal pyrolysis with slow heating rates and long residence times of the solid material and the volatiles in the hot reactor [1 - 8]. Most of this work was done in fixed bed reactors or in laboratory retorts. The objective was the optimization of the quality and yield of coke. Extensive understanding of the structure of coal and of the products of the carbonization process was obtained through these studies.

Several standard laboratory methods were developed in connection with the pyrolysis processes. These include the Fischer Assay (originally called the Fischer-Schrader Assay, developed in 1920) [45], the Bureau of Mines - American Gas Association Method [6] and the Gray-King Assay. These are used to determine carbonization properties and the volatile matter content of the coal. Each employs slow heating rates with maximum temperatures between 500 and 900 C, with no sweep gas used to remove the pyrolysis products. As a result, none of these can prevent secondary reactions between the volatiles and the coke.

Following the discovery in 1964 by Loison and Chauvin [9] that rapid heating of the coal results in a higher volatile yield than expected on the basis of an ASTM proximate analysis [44], new coal pyrolysis processes have been studied and a better understanding of the process has been obtained.

Studies of the pyrolysis process in pulverized coal flames have yielded information on the effects of rapid heating rates [10 - 13]. Small particles (< 100 μ m) and heating rates up to $5 \cdot 10^5$ C/sec were used in the reported tests. Meanwhile, interest in coal conversion was growing at this time (mid 1960's) and the objective was now to maximize the tar and gas yields [14 - 17]. These processes are characterized by residence times of the product gases of less than 1 minute and high heating rates of the coal particles. The coal is devolatilized in fluidized beds or entrained beds and a carrier gas is used to rapidly sweep the volatiles out of the reactor.

Several authors have previously proposed different reaction schemes to describe the kinetics of coal pyrolysis. Just as in the general literature on coal pyrolysis, these models can be divided into two classes :

- a) Models for slow pyrolysis : heating rate less than 10^{-2} C/sec or low final temperature (< 600 C)
- b) Models for fast pyrolysis : heating rate higher than 100 C/sec and high final temperature (> 600 C)

Probably the first chemical model in terms of a complex of chemical reactions was formulated by van Krevelen et. al. in 1956 [1,3]. They proposed the following overall scheme:



They did not incorporate any secondary reactions, although their experimental data were from slow carbonization processes, where

secondary reactions certainly occur. Van Krevelen proposed this scheme as a " mathematical model " with many simplifications, but with the potential to explain, at least qualitatively, many of the phenomena observed in a carbonization process. His main concern was the softening of the coal, without being as concerned with predicting yields. He assumed first-order reactions with an Arrhenius type rate law. Because of the simplicity of this model, it gave only qualitative results and was applicable only to a small temperature range and low heating rates.

Hill and Wiser at the University of Utah [18,19] conducted a series of long duration (up to 10 hours), low temperature pyrolysis experiments. They observed three regions with different reaction orders. In the first 60 minutes the rate of the reaction was approximately of the second order. This period was followed by a first order period for about 100 minutes. The last region was found to be controlled by a zero order rate law. This sequence was interpreted in terms of six chemical reactions, that have been formulated with molecular compounds. This mechanism is based on experimental data for only these slow processes, and it is not applicable to fast processes.

Berkowitz [8] obtained similar data for slow experiments and concluded, that for the conditions of his experiments the rate determining step of the pyrolytic reaction was the diffusion of the volatile matter out of the coal particle. Later, however, Pitt [5] used his own experimental data and the data of Berkowitz to support a chemical model. Pitt interpreted coal as a mixture of many components that can decompose independently, following a first order reaction with a wide distribution of activation energies. Unfortunately, Pitt did not determine the weight loss directly, but used the remaining volatile matter in the char as a measure of the degree of decomposition. Furthermore, he used a fixed, arbitrary frequency factor of $1.6 \cdot 10^{13} \text{ sec}^{-1}$ in the Arrhenius formula to determine the distribution of the activation energies, which of course is an arbitrary constraint that affects the numerical values of the activation energies.

Between 1960 and 1970, Peters and Juentgen et.al. at the Bergbauforschung GmbH in Essen, Germany [2,20,22,23] did some extensive studies on the gas release of hydrocarbons during very slow carbonization. They found that this gas release can be modeled by many parallel first-order single reactions, i.e. by a first-order reaction complex with distributed activation energies and frequency factors. They postulated that the gas release occurs in a sequence of the following four steps [22]:

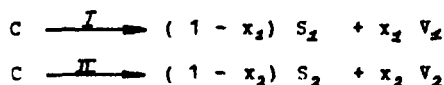
- A) thermal activation of the coal substance (equilibrium reaction)
- B) unimolecular reaction, bond scissions and formation of radicals
- C) reaction of two radicals to form a stable molecule
- D) diffusion of the molecule out of the particle

Figure 1 is a schematic representation of this process. The aromatic ring with aliphatic side chains represents the coal

structure.

Besides these models that deal only with slow processes, some models have been developed that can be applied to a fast pyrolysis process (heating rates 500 C/sec and up).

Kobayashi [24] used the data of Kimber and Gray [13] and Badzioch and Hawksley [11] to develop a kinetic model for the rapid decomposition of pulverized coal particles. His mechanism consisted of two competing first order reactions :



The kinetic values and the heats of reaction for these two reactions are given in Table I (Stickler et.al. found later in high temperature experiments that these heats of reactions are overestimated). This mechanism is applicable only for high heating rates (10^4 C/sec) and high temperatures (> 1000 K); it does not fit the slow, low temperature pyrolysis data.

Very recently Stickler et.al. [25] applied this scheme to model the gasification of pulverized coal in hot combustion gases. They added a physical gas flow and heat transport model, so that they were able to consider the heat-up of particles of different size classes. They used this model for comparison with experimental results for very high heating rates (10^5 C/sec) and high final temperatures (1700 K - 2300 K). In this limited range of operating conditions they only had a few experimental points to check the accuracy of this scheme.

Anthony wrote (1974) his Ph.D. Thesis on the kinetics of coal pyrolysis and hydrogasification [26]. He conducted experiments over a temperature range of 400 C to 1000 C and with heating rates varying from 10^2 to 10^4 C/sec. He found that the weight loss depends on the final temperature, but not on the heating rate. This led him to conclude that there are no concurrent, widely different competitive reactions. He therefore proposed a multiple reaction model with a statistically distributed activation energy, but with a constant frequency factor. For a bituminous coal he determined $E = 32.7 - 41.1$ kcal/mole and $A = 2.91 \cdot 10^3 \text{ sec}^{-1}$ at 1000 psia. He also introduced secondary deposition reactions for a " reactive " part of the volatile matter, which compete with the diffusive escape of the volatiles. He determined the ratio of the reaction rate of the secondary reactions to the overall mass transfer coefficient from experimental results and did not investigate these degradation reactions in detail. Neither Anthony nor Kobayashi, however, made any distinction between tar and gas in the volatile matter.

The numerical values for the kinetic parameters of the reaction scheme (activation energies, frequency factors, and stoichiometric coefficients) proposed in the present study were deduced in part by fitting the theoretical predictions with relevant data reported in the literature. In the present study, attention has been centered mainly

on the primary decomposition. Two sets of data were found to be the most suitable for this purpose : Curves obtained by Badzioch and Hawksley [11] at PCURA in Great Britain, and results from Peters and Juentgen [2] of Bergbau Forschung GmbH in Essen, Germany. Both research groups made their experiments with several coals of different rank. The results for two hvAb coals have been used in our present study. In the following, the work of these two groups will be discussed in detail.

3 Work Done by Badzioch and Hawksley at the British Coal Utilisation Research Association (PCURA)

Badzioch and Hawksley simulated the conditions in a pulverized coal flame, i.e. high heating rates (25000. - 50000. C/sec) and high temperatures (650 C - 950 C). They used pulverized coal with a mean particle size of about $20\mu\text{m}$. The experiments were carried out for ten different coals, from which we chose coal D, which is an hvAb coal with a composition similar to that of coal Fuerst Leopold used by Peters and Juentgen.

The experimental apparatus was a laminar flow furnace, which was heated to the desired temperature and through which a preheated flow of nitrogen was blown. The coal was then injected together with some cold nitrogen (in a dilute flow) into the hot main gas stream. The heat-up of the coal particle was rate-controlled by the mixing of the cold and the hot gases, which was found to take approximately 20 msec (for $20\mu\text{m}$ particles, thermal equilibration internally is fast compared with the fluid-mechanical mixing rate). The coal particles were collected and rapidly quenched after travelling a predetermined distance from the injector. This distance controlled the residence time of the particles in the furnace. The weight loss was determined by analysing the solid residue with respect to the ash content and the proximate volatile matter.

The qualitative results are :

1) The devolatilization products are richer in tars for this fast process than for a slow pyrolysis [10].

2) The weight loss exceeded the proximate volatile matter by a factor of 1.3 - 1.8, depending on the coal rank.

3) Even though the weight loss curve leveled off after about 100 msec (depending on the temperature) some residual volatile matter was found in the char.

They were able to fit the experimental results with an empirical relation for the weight loss as a function of time and temperature :

$$W = B_1 \cdot VM_0 \cdot (1 - B_3) \cdot (1 - \exp[-A \cdot t \cdot \exp(-B_2/T)]) \quad (1)$$

The devolatilization curves show that devolatilization starts about 20 msec after the injection, i.e. approximately at the end of the heat-up period. The time scale used in the equation therefore

starts 20 msec after injection. This indicates that the devolatilization during the heat-up period is only very small, and that the devolatilization occurs essentially at a constant temperature.

As Badzioch and Hawksley pointed out, the experimental conditions were chosen such that it might be safely assumed that only primary decomposition took place and that no secondary degradation of the tars occurred. This was mainly achieved by the short residence times, the high sweep gas-to-coal mass flow ratio, and the small particles. Additional experiments with larger particles (up to $60\mu\text{m}$) showed no effect of the particle size on the devolatilization. This indicates that the heat and mass transport processes are not rate controlling for these experimental conditions.

Despite the complexity of the processes during the heat-up period (mixing and heat conduction), we assumed in our modeling constant heating rates for each case. However, in order to reach the final temperature after 20 msec, the heating rate had to be adjusted to each final temperature.

Unfortunately, the theoretical results obtained by the proposed mechanism could not be compared directly with the experimental points of coal D, the one we had selected, since in ref. [11] only the experimental points for a coal B are reported. Therefore the comparison will be made between the curve we calculated using equation 1 with the empirical values given for coal D, and the theoretical results obtained with our own kinetic scheme.

C Work done by Peters and Juentgen at the Bergbauforschung GmbH, Germany (BBF)

Peters, Juentgen, and colleagues approached the problem of coal pyrolysis kinetics from two sides. First, they formulated a kinetic theory for non-isothermal experiments with thermal degradation reaction, where the temperature increases linearly with time [30,31,32]. They made some parametric studies to determine the changes in the gas release rate as a function of temperature, if the activation energy, the frequency factor, the heating rate or the final temperature are varied. They derived a very useful expression [32] that correlates the heating rate α and the temperature T_m at which maximum gas release occurred:

$$\ln \left[\left(\frac{\alpha}{T_m^2} \right) \left(\frac{E}{RA} \right) \right] = - \frac{E}{RT_m} \quad (2)$$

This equation, which was derived for a first-order, Arrhenius type rate law, gives a linear relation between $\ln(\alpha/T_m^2)$ and $1/T_m$, if the reaction mechanism remains the same over a certain range of heating rates.

The structure of coal is very irregular, and the bonds that have to be broken to release volatile matter do not have the same bond energies because they are differently influenced by the surrounding atoms. This influences the activation energies which are closely coupled with the bond energies. Therefore, the concept of reaction complexes was introduced, where a certain distribution of activation energies and frequency factors is used to describe the rate of a reaction [2]. This model has been used successfully also by other investigators [26,23].

In the experimental work done at BZF [2,21] the gas release rate of hydrocarbons (CH_4 up to C_3) was measured for various heating rates (10^{-4} to 10^{+3} C/sec) for different coals. For the comparison with our model the results for the coal Fuerst Leopold, a hvAb coal, was used.

The main results can be summarized as follows:

A) For all hydrocarbons a linear relation between $\ln(r/T_m^2)$ and $1/T_m$ was found over the whole range of heating rates that was investigated. This led to the conclusion that the mechanism for the production of these species does not change for these heating rates and temperatures.

B) The best fit of the experimental yield versus temperature curves for the higher hydrocarbons (C_2 and up) was obtained by using a rate law with a distributed activation energy and frequency factor (reaction complex). It was also possible to obtain kinetic values for the case of a single reaction (discrete activation energy), but there the agreement between the experimental and the theoretical curves was not as good as for a reaction complex.

Besides these two major works done at BCURA and BZF, information from other publications has been used to obtain a better picture of the process and to justify certain numbers or certain relations between different parameters (see sections 4 and 9).

3. General Scheme For Coal Pyrolysis

The reaction scheme which we want to propose should be applicable over a wide range of parameters, representing if possible all important parameters in real commercial systems. Following are some of the observed trends which should be reflected in such a model.

1.) Yields of volatile matter increase with increased final temperature of the process [26,27,16],

2.) Yields of volatile matter increase with increasing heating rates [10,11,12,16],

3.) Slow heating rates (carbonization processes) yield less tar than fast devolatilization processes,

4.) Increasing bed height in a fixed bed reactor decreases the yield of volatile matter [4,28],

5.) Tar vapors can be cracked at temperatures above 600 C

[14, 15, 29, 27, 30],

6.) Increasing particle size decreases the tar yield,

7.) The yield of the various classes of products vary with pressure in the reactor, in ways that depend on the type.

It is possible that items (4) and (6) are, in part, related to items (1), (2), and (3), but there may be additional factors not encompassed by the earlier noted trends, which cause these macroscopic trends. The effects (4), (6), and (7) are a result of the interplay between chemical kinetics, heat and mass transport processes, and fluid flow processes. In the BCUR and BBF works, these effects were minimized in the design of the pyrolysis experiments, in order to bring out particularly the purely chemical-kinetic results, (1), (2), (3), and (5).

Our first attempts have been directed toward simulating most of the above noted trends or characteristics. The reactions will be formulated in terms of generalized compounds, similar to van Krevelen's scheme, which did not attempt to specify the chemical constituents of each type of product.

Based on these findings and various weight loss curves reported in the literature, a general kinetic scheme for coal pyrolysis can be postulated (Table II). Even this scheme, more elaborate than that of van Krevelen, can only be a very simplified picture of the real process, due to the limited number of reactions and of classes of products and reactants.

This scheme can be divided into five main parts:

1.) Activation step (reaction 1) : The coal molecule is activated, bond scissions will occur, and radicals and smaller fragments of the original coal structure are produced.

2.) Primary decomposition (reactions 2 - 5) : the activated coal undergoes further reactions (additional bond breaking, radical recombination reactions, etc.) to form the primary volatile matter (primary tar and primary gas).

3.) Deactivation step (reaction 6) : At low temperatures, where the primary decomposition reactions are still very slow, part of the activated coal may deactivate again. This deactivation will probably not be simply the reverse reaction to the activation step, since it is very unlikely that, once the complex coal structure is broken up, the fragments will recombine to exactly the same structure. Probably the deactivated coal will have a more stable structure than the original coal.

4.) Reaction 7 and reaction 8 : the liquid primary tar has two routes to go. If sufficient heat is supplied it can vaporize (inside the particle or at the surface). If, however, the heat flux, i.e. the vaporization rate, is very slow, then the liquid primary tar (which is not a very stable molecule) can follow the competing reaction 7 and polymerize inside the particle. This polymerization will probably yield some secondary gas as well as augment the char.

5.) Gas phase degradation (reaction 9 and 10) : that portion of the tar that has vaporized and diffused out through the coal pores, can undergo secondary decomposition reaction in the hot reactor, until

it is swept out and quenched. These reactions are probably catalyzed at the surface of the coal particles. This degradation can be divided into two reactions: reaction 9 describes the polymerization in the gas phase and reaction 10 the cracking of the primary tar.

The gas phase degradation reactions 9 and 10 from primary tar to just a secondary gas and a solid residue, are certainly very simplified. Some of the tar will actually degrade to a liquid secondary product (i.e. light oils), and surely the primary gas can be cracked further. At present it does not seem reasonable to add more complexity to the degradation, since it is very difficult to divide experimental results into effects due to the primary decomposition and into effects due to the secondary degradation.

This general scheme, however, had to be simplified in order to assign kinetic values to the different reactions, because of the limited experimental data. Therefore the following simplifications were introduced:

- Very small particles (i.e. physical processes like heat and mass diffusion are not rate controlling, because the characteristic diffusion time is small).
- Uniform temperature throughout the particle
- Instantaneous vaporization (i.e. no decomposition in the liquid phase).
- Time for deactivation negligible.

This means that the heat transfer and mass diffusion processes are set aside in the fitting of our model to the available data. These simplifications will, of course, limit the applicability of the reduced kinetic scheme to cases involving small particles.

The last assumption had to be made for the following reasons: The deactivation occurs mainly in low temperature processes. In these processes, the degradation of the liquid tars will also be appreciable, because the vaporization rate will be slow. Both reactions occur inside the particle and decrease the yield of volatile matter. There are no experimental data available that would indicate how much of the decrease in volatile matter yield is due to any of these two reactions. Therefore, if we neglect the liquid tar polymerization we will also have to be consistent and neglect the deactivation.

The above assumptions lead to the simplified scheme shown in Table III. This scheme consists of three parts:

- A) activation step
- B) primary decomposition to gaseous primary tar and primary gas (reactions 2 - 5).
- C) secondary degradation of the primary tar in the gas phase (reactions 6 - 7).

In the remainder of the text the term primary decomposition generally will include the activation step.

4. Primary Decomposition

The main part of this paper will be concerned with the primary decomposition (i.e. reactions 1 - 5 of the simplified scheme, Table II). For this part of the scheme numerical values for the kinetic parameters have been obtained by fitting the theoretical curves to the data reported in the literature cited above. In the BCUPA and REF tests, the degradation of the released volatiles was presumably negligible, so reactions 6 and 7 played little role. First, however, the reasoning that led to each of the reactions 1 to 5 will be briefly summarized.

These five reactions form a model for the primary decomposition of coal. The initial activation step is followed by two parallel sequences for the decomposition of the activated coal: a low activation energy sequence, consisting of reactions 2 and 4, which will be favored at low temperatures, and a high activation energy sequence (reactions 3 and 5) for high temperature processes.

Reaction 1 :

At the beginning of our work, several different reaction schemes had been formulated that consisted of several decomposition reactions (similar to reactions 2 - 5), but without the activation step. The kinetic numbers had been selected to fit the BCUPA results [11]. However, it was found that these schemes could not be applied to slow carbonization processes with heating rates of 10^{-2} C/sec and slower, because in the theoretical predictions of these slow processes the coal would then decompose between 100 C and 200 C. That is, the reaction rates of the low activation energy decomposition reactions, adjusted to the fast processes, turn out to be much too fast at these low temperatures.

Therefore the activation step with a high activation energy was introduced. This reaction, interpreted as bond-breaking, provides an energy barrier for processes at low and medium temperatures, while it is no longer rate controlling at high temperatures.

Reaction 2 and 3 :

After the raw coal is converted to "activated coal", it can undergo two different reactions, depending on the temperature. One is a low activation energy reaction forming tar (reaction 2), and the other is a higher activation energy reaction forming primary gas. These two reactions also produce intermediate solids, S_1 and S_2 , respectively. They had to be introduced because it was found by many investigators that the ratio of gas/tar yields increases with increasing temperature. The tar forming reaction must have the lowest activation energy of all reactions, since throughout the literature the tar is reported to be driven off first in a pyrolysis process.

Reaction 2 :

Many slow carbonization experiments [2,4,19] report gas evolution up to high temperatures (600 C - 800 C), which means that this gas producing reaction must have a high activation energy. Since it is very likely that for these processes all activated coal follows reaction 2, we have to provide a succeeding reaction of the intermediate solid S_1 to produce primary gas. As suggested by Juentgen [2] in connection with the formation of CH_4 , this gas formation may result from several reactions. But in order to keep the mathematical approach tractable, we have introduced only reaction 4 in addition to reaction 2 in the low temperature sequence. Limiting the primary decomposition scheme at low temperatures in this way to only one gas forming reaction (reaction 4) cuts off the gas evolution at lower temperatures than observed. This is a minor defect in the model at this time which can be remedied if desired.

Reaction 5 :

Ladziach and Hawksley [11] found that even at 950 C some volatile matter is left in the coal after 100 msec which can be driven off the coal by a comparatively long-duration proximate analysis. This volatile matter remained in the coal even when the weight loss curve measured in the high temperature experiment showed a clear levelling off after about 40 msec. Kimber and Gray [13] on the other hand found that no volatile matter is left in the coke after the same time period, when the decomposition temperature was 1800 C. This indicates that there is another high activation energy reaction that produces gas from an intermediate solid. This is modelled by reaction 5.

5. Mathematical Description and Numerical Scheme

In order to formulate the differential equations that describe the decomposition as a function of time, we have to define the orders of the different reactions. In general, it would have been possible to formulate the equations with unknown reaction orders, but this would have added enormous complexity to the equations and to the numerical scheme to solve them. Fortunately, there are indications in the literature that can be used to select the reaction orders in advance.

Wiser et al. [19] observed a changing reaction order for low temperature experiments (400. C - 560. C), from second order at the beginning to zero order at the end of the experiment. On the other hand, many investigators suggested first order laws. Badzioch and Hawksley [11] obtained a very good fit of their high temperature experiments with a single first order equation. Peters and Juentgen [2,21], Pitt [5], Anthony [26], and Pennhack [33] also used first order expressions. They introduced " reaction complexes " with a distributed activation energy and frequency factor.

In this reaction scheme we did not use distributed activation energies, in order to keep the mathematical procedure simple. However, it might be worthwhile to incorporate the reaction complexes later for two reasons :

1.) Good agreement between experimental and theoretical curves has been obtained by this method [22].

2.) The irregular coal structure suggests strongly the model of a reaction complex.

Since in our theoretical model the process at slow heating rates and/or low temperatures (< 600 C) is controlled by the activation step, this reaction was chosen to be of second order, based on the findings of Wiser et.al. The other reactions are assumed to be of first order, following the data reported for the fast processes. These assumptions about the order of the reactions lead to the following system of nonlinear ordinary differential equations for the primary decomposition:

$$dC/dt = -k_1 \cdot C^2$$

$$dAC/dt = k_1 C^2 - (k_2 + k_3) AC$$

$$dPT/dt = x_2 k_2 AC$$

$$dPG/dt = x_3 k_3 AC + x_4 k_4 S_1 + x_5 k_5 S_2$$

$$dS_1/dt = (1 - x_1) k_2 AC - k_4 S_1$$

$$dS_2/dt = (1 - x_3) k_3 AC - k_5 S_2$$

$$dS_3/dt = (1 - x_4) k_4 S_1$$

$$dS_4/dt = (1 - x_5) k_5 S_2$$

3

Since reaction 1 is a second order reaction the system is nonlinear. Therefore, even for a constant temperature process, this system cannot be solved algebraically in closed form. A step-wise finite difference scheme was selected to solve the system numerically for a given temperature-time curve. The scheme is an implicit integration method that has been developed specifically for chemical kinetic problems (i.e. stiff differential equations) [34]. The integration method is of second order. The error in each time step is calculated using the neglected third order term. This error is then used to control the step size. A detailed description of the numerical scheme is given in [34].

6. Selection of the Kinetic Parameters

A Stoichiometric Coefficients

Since all the primary decomposition reactions have a solid as the

reactant, the structure and molecular weight of which are unknown, the stoichiometric coefficients are defined as mass stoichiometric coefficients.

The maximum possible tar yield is given by x_2 . If all coal follows the low temperature route (up to about 700 C) then x_2 is equal to the yield of primary tar. For most of the fast processes (e.g. fluidized beds) tar yields of between 20 % and 30 % are reported. But recently Sass [37] and Mentser et.al. [35,36] reported yields of up to 36 % and 40 %, respectively. Therefore x_2 was chosen as 0.4.

Badzioch and Hawksley measured an overall weight loss of 49 %. This indicates that the low temperature gas forming reaction must yield 9 % gas, which corresponds to $x_4 = 0.15$. This is supported by Mentser [35] who found a gas yield of 9 % at 700 C (together with 40 % tar).

The high temperature route consists of reactions 3 and 5. Since under the fast BCURA conditions, reaction 5 does not contribute any gas, reaction 3 must have a gas yield of approximately 50 %, i.e. $x_3 = 0.5$.

The highest volatile matter yields to date have been reported by Kimber and Gray [13] and Stickler [25]. Both found a maximum of about 72 % for very fast (10^5 C/sec) and very high temperature (2000 - 2500 C) experiments. If we assume, that at these temperatures and heating rates all coal decomposes via the high temperature route, then the stoichiometric coefficient for reaction 5 must be $x_5 = 0.4$, in order to yield 70 % volatile matter.

B Activation Energies and Frequency Factors

Reaction 1 :

This reaction is the activation step, which prevents the coal from decomposing at low temperatures in a slow heating process. The reaction is of second order, hence the rate law has the following form (equation 3):

$$dC/dt = -k_1 C^2 = -A_1 \exp(-E_1/RT) \cdot C^2$$

When the rate constants were determined, reaction 1 was still considered to be of first order. But the principal reasoning for obtaining the kinetic values does not change if we go to a second order expression. Therefore the derivation of the numbers using a first order rate law will be presented here. The numerical results show that the change in reaction order did not require a change of the kinetic values.

The reason for starting with a system of first order reactions

was to simplify the mathematical procedure. The system of ordinary differential equations, that describe the changes in concentrations for such a reaction scheme, is linear and therefore can be solved analytically for a constant temperature. This then has a big advantage in terms of computing time and accuracy of the numerical results.

As mentioned earlier, reaction 1 has to satisfy two conditions:

- A) Serve as an energy barrier to prevent early decomposition (at temperatures $< 200^\circ \text{C}$) for slow processes. (BDF data [2,21] was used to check this).
- B) High reaction rates at temperatures above 650°C , to allow fast processes like the BCUFA experiments.

Using basic kinetic principals, Peters et.al. [22] derived a formula for the gas release of a thermal degradation reaction (for constant heating rate and a first order rate law). This relation can be written in terms of the decomposition rate of the undecomposed coal C :

$$\frac{C}{C_0} = \exp \left[-\frac{A}{m} \cdot \frac{RT^2}{E} \cdot e^{-\frac{E}{RT}} \right] \quad \left(= \frac{V_0 - V}{V_0} \right) \quad (4)$$

where the term C/C_0 is equivalent to the term $(V_0 - V)/V_0$ that has been used by Peters to characterize the degree of decomposition.

From the BDF results we obtain the following characteristic temperatures [2]:

$m = 4.2 \cdot 10^{-4} \text{ C/sec}$	$T_m = 360.^\circ \text{C}$
$m = 4.3 \cdot 10^{-3} \text{ C/sec}$	$T_m = 400.^\circ \text{C}$
$m = 1.5 \cdot 10^{-2} \text{ C/sec}$	$T_m = 430.^\circ \text{C}$

where T_m is the temperature at which the maximum gas release rate is measured (this occurs when about 50 % or more coal is decomposed). This implies that at $T = T_m$ about 30 % to 50 % of the coal should be decomposed.

The second condition implies, that the activation should be essentially complete after the heat-up period of 20 msec. This gives $C/C_0 \approx 0.05$ for $m = 35000. - 50000. \text{ C/sec}$ after $t = 20 \text{ msec}$

Using equation 4, we can now calculate the value for C/C_0 for these different heating rates using several pairs of A_1 and E_1 and then select those values that promise the best fit. The results are shown in Table IV.

The values for C/C_0 for $m = 4.3 \cdot 10^{-3} \text{ C/sec}$ are always somewhat lower than they should be, or than the values for $m = 4.2 \cdot 10^{-4} \text{ C/sec}$ or $1.5 \cdot 10^{-2} \text{ C/sec}$. This is because the temperature, T_m , cannot be determined exactly enough from the graphs in [2]. A small correction in T_m (decrease) would bring the results into the right range.

The results for $E_1 = 70$ kcal/mole show that the decomposition at the high temperatures is too slow, while for $E_1 = 80$ kcal/mole the energy barrier is too high for the slow heating processes. Therefore a value of $E_1 = 75$ kcal/mole has been selected and the corresponding frequency factor has been determined to satisfy the two conditions.

The slow decomposition results should not change appreciably when we assume a second order rate law for the activation step, because only that part of the process in which the coal mass fraction is greater than 0.5 was considered. The major difference in the behavior of a second order reaction compared to a first order reaction occurs, however, when the mass fractions are small (< 0.25). For the high temperature process, the difference resulting from a first order and a second order rate law is shown in Figure 2. It shows the decrease of the coal mass fraction for two temperatures (973 K, 1223 K). This figure indicates very clearly that for $T=973$ K a small difference in the degree of conversion at 20 msec is expected, while for $T = 1223$ K, even with the second order reaction, all coal is converted well before $t = 20$ msec.

Therefore, the two conditions that were used to derive the kinetic values for the activation step are also satisfied with a second order reaction, without any change in the kinetic values themselves.

Reaction 2 and 3 :

The reaction rates of the reactions 2 and 3 are based only on the BCURA results, because these are the only data, for which secondary degradation is insignificant. These data also have one big disadvantage, however, because only the overall volatile matter loss is reported and no distinction between tar and gas is made.

To obtain kinetic values, the initial slopes of several BCURA curves (at different temperatures) were used. The initial production rate of BCURA is :

$$dW/dt = D \cdot A \cdot \exp(-E_2/T) \quad (5)$$

Using the appropriate empirical constants for coal D (given in [11]), we obtain for the different temperatures:

T (K)	973	1023	1073	1123	1173	1223
dW/dt (sec ⁻¹)	7.02	10.98	16.47	23.93	33.41	45.56

This initial weight loss of BCURA will be set equal to the weight loss predicted by our reaction scheme at 20 msec. If we assume that at 20 msec the decomposition just starts, then no solids S_1 and S_2 have formed yet and the reactions 4 and 5 do not contribute to the weight loss. Therefore the " initial " weight loss can be approximated as follows :

$$dW/dt = x_2 k_2 AC^* + x_3 k_3 AC^*$$

(6)

where AC^* is the mass fraction of activated coal at $t = 20$ msec, which is determined from the activation reaction at 20 msec. These values can be obtained using equation 4 together with the different heating rates and final temperatures, resulting in :

T (K)	973	1023	1073	1123	1223
AC	.84	1.00	1.00	1.00	1.00

If it is assumed that for $T = 973$ K and $T = 1023$ K all coal converts through reaction 2, the activation energy and the frequency factor of reaction 2 can be calculated using equation 6. This gives

$$\begin{aligned} A_2 &= 5501. \text{ sec}^{-2} \\ E_2 &= 10.768 \text{ kcal/mole} \end{aligned}$$

To obtain the kinetic values for reaction 3, the initial weight loss at $T = 1123$ K and $T = 1223$ K is matched with the analytic expression. At these temperatures both reactions (reaction 2 and 3) contribute. This calculation then leads to

$$\begin{aligned} A_3 &= 3.4 \cdot 10^6 \text{ sec}^{-2} \\ E_3 &= 31.06 \text{ kcal/mole} \end{aligned}$$

These values however, result in too high a reaction rate at $T = 973$ K. To reduce the reaction rate at $T = 973$ K, and to simultaneously keep the rates high at $T = 1100 - 1200$ K, the activation energy E_3 had to be increased. Small changes in the frequency factor A_2 also improved the fit. Finally the best results were obtained for

$$\begin{aligned} A_2 &= 4.5 \cdot 10^3 \text{ sec}^{-2} & A_3 &= 3 \cdot 10^6 \text{ sec}^{-2} \\ E_2 &= 10.7 \text{ kcal/mole} & E_3 &= 40. \text{ kcal/mole} \end{aligned}$$

All this was done for a first order activation step. The introduction of a second order activation step did change the results only by about 1/2 %, which is well within the limits of the accuracy of the BCURA data.

The big uncertainty in these values however is the assumption that at $T = 973$ K and 1023 K all activated coal decomposes via the low temperature route. Since Badzioch and Hawksley did not report any tar or gas yields, this assumption cannot be verified at the moment. Other yield curves indicate that the maximum tar yield is reached between 600 - 700 C [27,35]. But in these experiments secondary decomposition cannot be excluded. However, it will be shown that by choosing another set of kinetic values for reactions 2 and 3, the overall PCUFA curves and different tar/gas ratios can be predicted.

In order to increase the gas yield and decrease the tar yield, both activation energies had to be lowered. An activation energy, $E_2 = 3$ kcal/mole, was arbitrarily chosen and the other values were

determined again by matching the initial slopes. No real optimization was carried out, but the fit with the BCURA curves was reasonably good for

$$E_2 = 5. \text{ kcal/mole}$$

$$E_3 = 30. \text{ kcal/mole}$$

Figure 3 shows the tar and gas yields as a function of temperature for a devolatilization process of 100 msec duration. It is now clear from this figure, that the primary decomposition scheme can easily be adjusted (if necessary) to new experimental data which reports the primary tar and the primary gas yields separately.

Reaction 4 :

Modeling the slow heating process of BPF means that all activated coal decomposes via reactions 2 and 4 . Therefore, the only gas forming reaction is reaction 4 and the results of Peters and Joestgen for the gas production have to be matched by reaction 4 . As mentioned earlier, it will probably not be possible to fit the whole shape of the gas release curve, but the changes of the temperature T_m with changing heating rates can be simulated. Figure 4 shows the results for

$$A_4 = 1.7 \cdot 10^{13} \text{ sec}^{-1}$$

$$E_4 = 55. \text{ kcal/mole}$$

and the comparison with the BPF curves. Figure 5 shows the influence of the kinetic values for reaction 4 on the relation between the temperature T_m and the heating rate π . The corresponding pairs of A_4 and E_4 have been selected to obtain a good fit with the BCURA curves.

Reaction 5 :

The kinetic values for this reaction have been chosen rather arbitrarily. Due to the scarcity of experimental data for high temperature ($> 1300 \text{ K}$), short duration processes (Kirber and Gray only reported about ten experimental points at different temperatures), no detailed analysis of the influence of this reaction has been made.

The activation energy of 55 kcal/mole was chosen arbitrarily and the frequency factor determined, so that at the experimental conditions of Padzioch and Hawksley no appreciable degradation of S_2 to S_4 took place. This was necessary to explain the residual volatile matter found in their experiments.

7. Agreement With the Experimental Data

The following numbers for the stoichiometric coefficients, the

activation energies, and the frequency factors have been found to give the best agreement with the experimental data:

Reaction	x	A (sec ⁻¹)	E (kcal/mole)
1	1.0	$2.0 \cdot 10^{20}$	75.
2	0.4	$4.5 \cdot 10^3$	10.7
3	0.5	$3.0 \cdot 10^8$	40.
4	0.15	$1.7 \cdot 10^{13}$	55.
5	0.4	$1.0 \cdot 10^{10}$	55.

A Comparison With BCURA Results

Figure 6 give a comparison between the theoretical BCURA volatile matter yield curves and the predicted curves obtained from the primary decomposition scheme for six different temperatures.

By fitting their results with one single rate expression, Badzioch and Hawksley [11] assumed that no appreciable decomposition had taken place during the heat-up period. They found the heat-up time to be about 20 msec. Only after this 20 msec, the decomposition proceeds at a constant temperature, which they use in their rate expression. The starting point for the decomposition was determined by extrapolating the curve through the actually measured points to the line where the weight loss was zero. The data points were taken only at $t = 30$ msec and later. This extrapolation, however, might not represent the true devolatilization curve at these early times.

With the proposed mechanism the heat-up period must be included because of the activation step (reaction 1) which is fast at temperatures above 600 C. Therefore the results obtained by our scheme already show some decomposition in the first 20 msec, depending on the temperature. This probably is a better representation of the true devolatilization curves than the BCURA curves.

The curves show a very good agreement for $t > 30$ msec and the differences between the present predictions and the BCURA curves are not more than 1.5 %. This is certainly less than the error between the empirical BCURA curves and the actual data points, as obtained in the experiment.

Figures 7 and 8 give an indication of the concentration variations versus time for the different compounds and two different temperatures. The rapid decrease of the C mass fraction and the corresponding increase in AC should be noted. This shows that under these rapid heating, high temperature conditions the activation step is not rate controlling, but goes to completion during the heat-up period.

3 Comparison With PBT Results

Peters and Juentgen [21] found, that their experimental results for a heating rate range of 10^{-4} C/sec to 10^{-3} C/sec gave a straight line for each hydrocarbon species. The curves for methane and ethane were used for comparison with our kinetic scheme, since all the other curves lie between these two. The results are shown in Figure 4. The heating rates that are covered in this graph are $m = 10^{-4}$ C/sec at $1/T_m = 1.5 \cdot 10^{-3}$ K $^{-1}$ and $m = 10^{-3}$ C/sec for $1/T_m = 10^{-3}$ K $^{-1}$. The corresponding temperatures are 393.C and 727.C, respectively.

3 Some Comments About The Reaction Constants

Figure 9 shows the reaction constants for the five reactions versus $1/T$ (Arrhenius plot). The following characteristics can be observed.

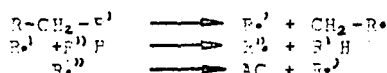
Reaction 1 is rate controlling up to about 800 K. Up to this temperature, all activated coal is immediately converted to primary tar and the intermediate solid S_1 , since, (a) reaction 2 is much faster than reaction 1, and (b) reaction 3 (which is the second possibility for the decomposition of activated coal) is even slower than reaction 1. Above 850 K, activated coal is accumulated, since the succeeding reactions are slower than the activation step. Comparison of the two parallel reactions 2 and 3, that follow the activation step shows that the tar formation is favored up to temperatures of 1300 K, at which temperature the reaction rates are approximately equal. Up to around 1000 K reaction 4 is slower than the preceding reaction 2, therefore an accumulation of solid S_2 occurs. This will result in the gas release occurring after the tar release, which is observed in all devolatilization experiments. The rates of reaction 3 and 5 are equal at about 2000 K.

8. Chemical Interpretation of the Activation Step

The mechanism and rate of coal pyrolysis depend, of course, on the molecular structure of coal. Coal is a polymeric compound (or perhaps a mixture of such compounds) containing polynuclear aromatic, aliphatic, and some heterocyclic groups. While there is some disagreement about the precise structure (for example the number and length of the aliphatic chains that sometimes link aromatic and acyclic systems [39,40,41]) some general features can be agreed upon. In particular it seems that coal contains a polymeric molecule (or molecules) having C-C, C-H, C-S, C-N, C-O, OH, and EE bonds (in varying degree of saturation), but that there are no unstable three or four member ring structures.

Some conclusions about the mechanism of the activation step can be drawn from this limited information. First, in order to form a low molecular weight hydrocarbon fraction, carbon-carbon bonds must be broken at some point in the mechanism. This fact is consistent with the high activation energy proposed for the activation step. The activation energy for simple C-C bond scission must be of the order of the bond energy, which is about 85 kcal/mole (for C_2H_6 it is 85 kcal/mole; for $C_4H_{10} \rightarrow 2 C_2H_5$, it is 82 kcal/mole) [42]. For elimination of ethylene in simultaneous rupture of two carbon-carbon bonds, activation energies of 65 kcal/mole are typical for six-membered ring systems.

It was shown that the only acceptable value for the pre-exponential factor for the rate constant was $2 \cdot 10^{20} \text{ sec}^{-1}$, whereas the largest measured frequency factors for bond scissions are of the order of $10^{12.5} \text{ sec}^{-1}$ [42]. However for the degradation of polytetrafluoroethylene (teflon) a frequency factor of about 10^{19} sec^{-1} was measured [43] and a complex radical mechanism in the solid phase was proposed for this process. Therefore, the activation step may involve not a single elementary reaction, but a complex radical mechanism with chain reactions, such as the following example

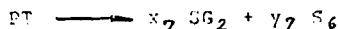


where R, R', R'' denote functional groups in the coal structure. A similar mechanism has been proposed by Wiser et.al. [19].

9. Secondary Decomposition

It is much more difficult to obtain and interpret experimental data about the secondary decomposition than it is for the primary decomposition, because the effects of the secondary degradation are always coupled and/or covered by the effects of the primary decomposition. But there is some, mostly qualitative, information available that can be used to support a secondary decomposition model consisting of two gas phase reactions.

Peters [22] investigated the differences between the tars from a low temperature carbonization and from a high temperature, fast pyrolysis. He cracked the high temperature tars and found that the cracking products were substantially different from the low temperature tars. Since a low temperature carbonization is a very slow process, the volatile matter that is driven off here is to a large extent the product of a secondary degradation. The difference in the products from a slow process and the cracking products of high temperature tar then indicates that there must be two different degradation reactions. Therefore, the two reactions 6 and 7 of the simplified scheme have been formulated:



The polymerization is a low activation energy reaction, while the cracking occurs at high temperatures (> 600 C), i.e. it has a high activation energy.

Some data has been reported in the literature that can be interpreted as the result of gas phase polymerization. Mazumdar [4] and Essenhigh et.al. [28] found a relationship between the depth of a fixed coal bed and the coke and volatile matter yields, respectively. Mazumdar used a slow heating process (Gray King Assay) while Essenhigh et.al. used heating rates between 16 C/sec and 20 C/sec. With increasing bed depth the coke yield increased, while the volatile matter yield decreased. Mazumdar found no evidence of any cracking reactions. Therefore the only explanation for these curves is the polymerization reaction in the gas phase. The deeper the bed, the longer the residence time of those vapors that originate from the lower levels, while the vapors from the top layers of the bed still can escape relatively unaltered. Mazumdar reports a decrease in tar yields from 15 % at " zero bed thickness " to 3 % in large coke ovens. This was accompanied by an increase of coke yield from 71.5 % up to about 78 %. This indicates that the polymerization degrades the tar to a solid and a gas (or light oil).

Not much data is reported in the literature on the cracking of the primary tars. However, at least one observation has been made by several investigators [14,15,27,29,30]: there is no appreciable cracking of tar vapors at temperatures below 600 C . In the normal temperature range of coal pyrolysis processes (< 1000 C) the gaseous hydrocarbons will not crack . Therefore we will only consider the thermal cracking of the primary tars.

In order to consider the secondary degradation reactions in our model, we have to formulate a mathematical model of the gas flow through the reactor. This is necessary to determine the residence time of the volatile matter that is released from the solid in the reactor.

Our present approach is directed towards the formulation of a very simple model to simulate the fixed-bed conditions that have been used by Essenhigh et.al. and Mazumdar to obtain their curves of volatile matter (or coke) yield as a function of the bed height. These two curves will be used to select the kinetic parameters for reactions 6 and 7.

The following simplifying assumptions have been made to formulate a mathematical model of the fixed bed reactor:

- no change in porosity (i.e. void space) during the decomposition of the coal particle
- no pressure drop ($p = \text{const.}$)
- specified temperature history (constant over x)
- constant cross section
- uniform distribution of the coal in the bed, hence constant gas

- and tar release rates over x
- temperature in the gas phase is equal to the uniform particle temperature
- diffusion in the gas phase can be neglected in comparison with the convective transport

This implies that the momentum and energy equation do not have to be utilized and only the conservation equations for mass and species need to be solved.

The gas and the tar production rates are calculated independently using the primary decomposition scheme and the given temperature-time curve. This separation is possible, because the primary degradation is not influenced by the secondary degradation.

The stoichiometric coefficients x and x for the two gas phase reactions are defined on a molar basis. Therefore, molecular weights have to be estimated for the gaseous species. The coefficients y and y for the production of solid material are defined as the number of grams of solid produced by the degradation of one mole of primary tar. It is not necessary to know the number of moles of solid (which would depend on the unknown molecular weight), since the material balance is not based on molar quantities.

For the non-steady gas flow through the bed the following conservation equations can be derived:

Mass Continuity

$$\frac{\partial S}{\partial t} + u \frac{\partial S}{\partial x} + S \frac{\partial u}{\partial x} = \frac{1}{y} (PR_T + PR_G) + RR_{solid} \quad (7)$$

Species Continuity

$$y_i \frac{\partial S}{\partial t} + S \frac{\partial y_i}{\partial t} + y_i S \frac{\partial u}{\partial x} + y_i u \frac{\partial S}{\partial x} + S u \frac{\partial y_i}{\partial x} = \frac{1}{y} PR_i + RR_i \quad (8)$$

Four species are present in the gas phase: primary tar, primary gas, secondary gas, and carrier gas (sweep gas). The carrier gas may be the fluidizing gas in a fluidized bed reactor or the transport gas in a transport reactor. It will be treated as an inert gas that only dilutes the volatiles and sweeps them out of the reactor.

The reaction rates that correspond to the two gas phase reactions, 6 and 7 are:

$$RR_{PT} = -(k_6 + k_7) Y_{PT}$$

$$RR_{SG} = (x_6 k_6 + x_7 k_7) Y_{PT} (M_{SG}/M_{PT})$$

$$RR_{solid} = -(y_6 k_6 + y_7 k_7) Y_{PT} (1/M_{PT})$$

$$RR_{PG} = RR_{CG} = 0.$$

Using equation 7, equation 8 reduces to the following system of coupled, non-linear partial differential equations :

$$\frac{\partial Y_i}{\partial t} + u \frac{\partial Y_i}{\partial x} = \frac{1}{S} \left\{ \frac{1}{v} PR_i + RR_i - Y_i \left(\frac{1}{v} [PR_T + PR_G] + RR_{solid} \right) \right\} \quad (9)$$

with $Y_i = Y_{PT}, Y_{PG}, Y_{SG}, Y_{CG}$

Under the assumption, that all gas phase components follow the ideal gas law, the following is true

$$S = \frac{P}{RT} \left(1 / \sum_{j=1}^k \frac{Y_j}{M_j} \right) \quad (10)$$

and with this equation of state the partial derivatives $\partial S / \partial t$ and $\partial S / \partial x$ in equation 7 can be eliminated and after some rearrangements an ordinary differential equation to calculate the velocity can be obtained:

$$\frac{du}{dx} = \frac{RT}{Pv} \left(\frac{PR_T}{M_{PT}} + \frac{PR_G}{M_{PG}} \right) + \left\{ (x_6 - 1)k_6 + (x_7 - 1)k_7 \right\} \frac{Y_{PT}}{M_{PT} \sum_{j=1}^k \frac{Y_j}{M_j}} + \frac{1}{T} \left(u \frac{\partial T}{\partial x} + \frac{\partial T}{\partial t} \right) \quad (11)$$

The system of partial differential equations will be solved numerically using a linear finite element method with a generalized implicit time marching procedure. The non-linear inhomogeneous terms will be quasilinearized using the first term of a Taylor-series expansion.

Kinetic values for the two degradation reactions will then be selected in order to obtain good agreement between the theoretical yields for different bed heights and the experimental data.

10. Summary and Conclusions

A kinetic model for coal pyrolysis has been developed that can be used for the theoretical optimization of coal conversion processes. In contrast to many previously proposed schemes, this model has been formulated in terms of general compounds like tars, gases, and solids, i.e. the volatile matter has been divided into liquid and gaseous products. Furthermore, a high activation energy step has been introduced to convert the raw coal to activated coal. With this activation step it is possible to apply the scheme over a wide range of temperatures and heating rates, unlike other schemes that have been limited to narrow ranges.

The proposed kinetic model consists an activation step, four primary decomposition reactions in the solid phase, and two degradation reactions in the gas phase. Good agreement between previously published experimental results and the theoretical predictions for primary decomposition has been obtained over a wide range of heating rates (10^{-4} to 10^{+5} C/sec) and, associated with it, over a wide range of temperatures (400 C to 950 C).

The kinetic model has been formulated and the kinetic parameters have been obtained for a high volatile A bituminous coal. However, with appropriate new numerical values for the stoichiometric coefficients, the activation energies, and the frequency factors, the scheme should also be applicable for coals of different ranks. In exception may be anthracite, because of its very low volatility. Following the procedure used for the hvbb coal, these new kinetic constants could be determined, especially since Badzioch and Marksley as well as Peters and Juergen did repeat their experiments for several coals of different ranks.

If kinetic parameters were available for different coals, these parameters probably could be correlated with some characteristic properties of the coal, e.g. the ultimate or the petrographic analysis. In this way the scheme would then become more broadly applicable for different coal ranks.

The work that has been done so far is only the first step towards a theoretical technique for optimizing coal conversion processes. However, the scheme gives a deeper understanding of the pyrolysis process and opens many options for additional work and applications.

A refinement of the scheme probably should include:

- 1) Addition of the degradation reaction of the liquid tar inside the particle and the deactivation of the activated coal. This was proposed above in the general scheme, but then had to be set aside because of the lack of experimental data against which to test the theory.

- 2) Characterization of the physical processes like tar vaporization, heat transfer to and inside the coal, and the diffusion of the volatile matter out of the coal particle. This would allow the investigation of the influences of bed height, pressure and particle size on yields and a determination of those conditions in which physical processes are rate controlling.

- 3) Identification of the general compounds (tar, gas, solid) in terms of chemical species in order to distinguish between more or less desirable pyrolysis products. This more detailed formulation of the reactions can also lead to the determination of the heats of reaction.

It will not be possible to accomplish these points by using only experimental data presently available in the open literature. To refine and extend our kinetic model, new experiments will have to be designed and conducted. However, our kinetic scheme helps to identify the important parameters that will have to be properly considered in new experiments. These parameters will include the identification of the volatile matter with respect to tars, gases and liquors, possibly even with respect to specific chemical species, and the effects of the particle size and the pressure.

The importance of a good chemical-kinetic (and thermochemical) scheme is that it can be applied to the theoretical modeling of coal conversion processes. This will include the coupling of the chemical kinetic model with models of flow reactors, such as fluidized beds, fixed beds (co-current or counter-current), and entrained flow

reactors. Because of the distinction between tars and different gases, our model is readily applicable for the optimization of coal liquefaction and coal gasification processes. With a further refinement of the model the possible goals for optimization can be extended, e.g. an optimization towards a maximum economic value of all the pyrolysis products would be possible. The reactor designer can use this kind of model also for controll calculations, i.e., how to achieve optimum yield or how to avoid undesired reactor instabilities (using the equations in dynamic form). Our approach to the modeling of the gas phase degradation is a first example (as described above) of the coupling of the chemical kinetic scheme with a simplified flow reactor model.

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NOMENCLATURE

- A = Frequency factor, sec^{-1}
 AC = Mass fraction of activated coal, $g_{AC}/g_{\text{Start.Material}}$
 $B_{1,2}$ = Empirical constants used by Badzioch
 B_3 = Residual volatile matter in the char
 C = Mass fraction of coal, $g_C/g_{\text{Start.Material}}$
 C_0 = Initial mass fraction of coal, $g_C/g_{\text{Start.Material}}$ (normally = 1)
 E = Activation energy, kcal/mole
 f_i = Rate at which compound i is produced or consumed, g_i/sec
 m = Heating rate, K/sec
 M_i = Molecular weight of gaseous species i , g/mole
 k_j = Rate constant of reaction j , sec^{-1}
 P = Pressure, g/cm^2
 PG = Mass fraction of primary gas, $g_{PG}/g_{\text{Start.Material}}$
 PR_i = Production rate of gaseous species i due to primary decomposition, $g_i/\text{cm}^3_{\text{Reactor}}\text{-sec}$
 PT = Mass fraction of primary tar, $g_{PT}/g_{\text{Start.Material}}$
 R = Gas constant, kcal/moleK
 RP_i = Reaction rate of species i in the gas phase, $g_i/\text{cm}^3_{\text{Gasphase}}\text{-sec}$
 S_i = Mass fraction of solid intermediate i or solid residue i , $g_S/g_{\text{Start.Material}}$
 t = Time, sec
 T = Temperature, K
 T_M = Temperature of maximum gas release rate, K
 u = Flow velocity in the gas phase, cm/sec
 V = Gas volume released by a thermal degradation reaction (varying with time), $\text{cm}^3/g_{\text{Mat}}$

- V_0 = Maximum possible gas volume from a thermal degradation reaction, $\text{cm}^3/\text{g}_{\text{Mat}}$
 VM = Mass fraction of volatile matter, $\text{g } VM/\text{g}_{\text{Start.Material}}$
 VM_0 = Proximate volatile matter (ASTM standard), %
 W = Weight loss
 x = Stoichiometric coefficient (by mass for reactions 1-5) (molar for reactions 6-7)
 y_i = Stoichiometric coefficient for the solid residue produced by the gas phase degradation.
 Y_i = Mass fraction of gaseous species i in the gas phase
 ρ = Density in the gas phase
 v = Void space in the gas phase

Table I

Kinetic parameters for the pyrolysis model
of Kobayashi (Ref. 25)

KINETIC PARAMETER	REACTION	
	I	II
Activation Energy E (kcal/mole)	17.6	60.0
Frequency Factor A (sec^{-1})	2.2×10^5	2.0×10^{12}
Stoichiometric Coefficient x	0.39	1.0
Heat of Reaction ΔH (cal/g coal)	-412.	-200.

TABLE II
GENERAL HYPOTHETICAL SCHEME FOR
COAL PYROLYSIS

C	k_1	AC	Activation Step (high E)
AC	k_2	$x_2 PT_L + (1 - x_2) S_1$	low E
AC	k_3	$x_3 PG_2 + (1 - x_3) S_2$	medium E
S_1	k_4	$x_4 PG_2 + (1 - x_4) S_3$	primary decomposition high E
S_2	k_5	$x_5 PG_3 + (1 - x_5) S_4$	high E
AC	k_6	DAC	Deactivation Step (DAC \neq C)
PT_L	k_7	$x_7 SG_1 + y_7 S_5$	Polymerization in the liquid phase inside the particle
PT_L	k_8	PT_G	Vaporization (depending on heat and mass diffusion)
PT_G	k_9	$x_9 SG_2 + y_9 S_6$	Polymerization in the gas phase
PT_G	k_{10}	$x_{10} SG_3 + y_{10} S_7$	Cracking in the gas phase

where

C = Initial coal
 AC = Activated coal
 PT_L = Liquid primary tar
 PT_G = Gaseous primary tar
 PG = Primary gas
 SG = Secondary gas
 S = Solid intermediate or residue
 x, y = Stoichiometric coefficients
 AE = Activation energy

TABLE III
SIMPLIFIED SCHEME FOR COAL PYROLYSIS

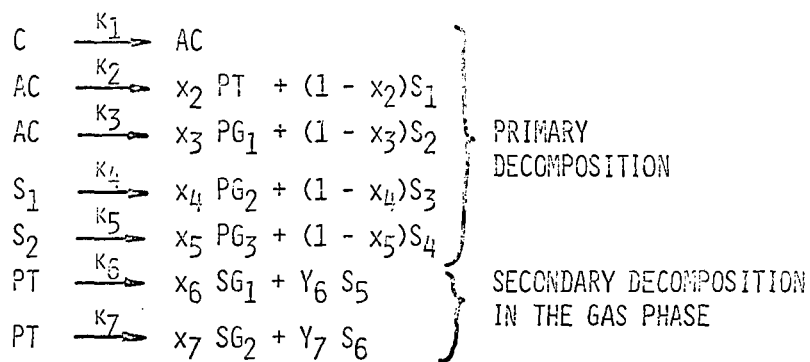


TABLE IV
SELECTION OF KINETIC VALUES FOR REACTION

E_1 (kcal/mole)	A_1 (sec ⁻¹)	m (C/sec)	T (K)	$\frac{C}{C_0} = \frac{V_0 - V}{V_0}$
70.	$3 \cdot 10^{18}$	$4.2 \cdot 10^{-5}$	633.	0.538
		$4.3 \cdot 10^{-4}$	673.	0.199
		$1.5 \cdot 10^{-2}$	703.	0.624
		35000.	973.	0.653
		45000.	1173.	0.0
75.	$2 \cdot 10^{20}$	$4.2 \cdot 10^{-5}$	633.	0.537
		$4.3 \cdot 10^{-4}$	673.	0.0925
		$1.5 \cdot 10^{-2}$	703.	0.442
		35000	973.	0.136
		45000	1173.	0.0
80.	$2.4 \cdot 10^{21}$	$4.2 \cdot 10^{-5}$	633.	0.877
		$4.3 \cdot 10^{-4}$	673.	0.530
		$1.5 \cdot 10^{-2}$	703.	0.774
		35000.	973.	0.185
		45000	1173.	0.0

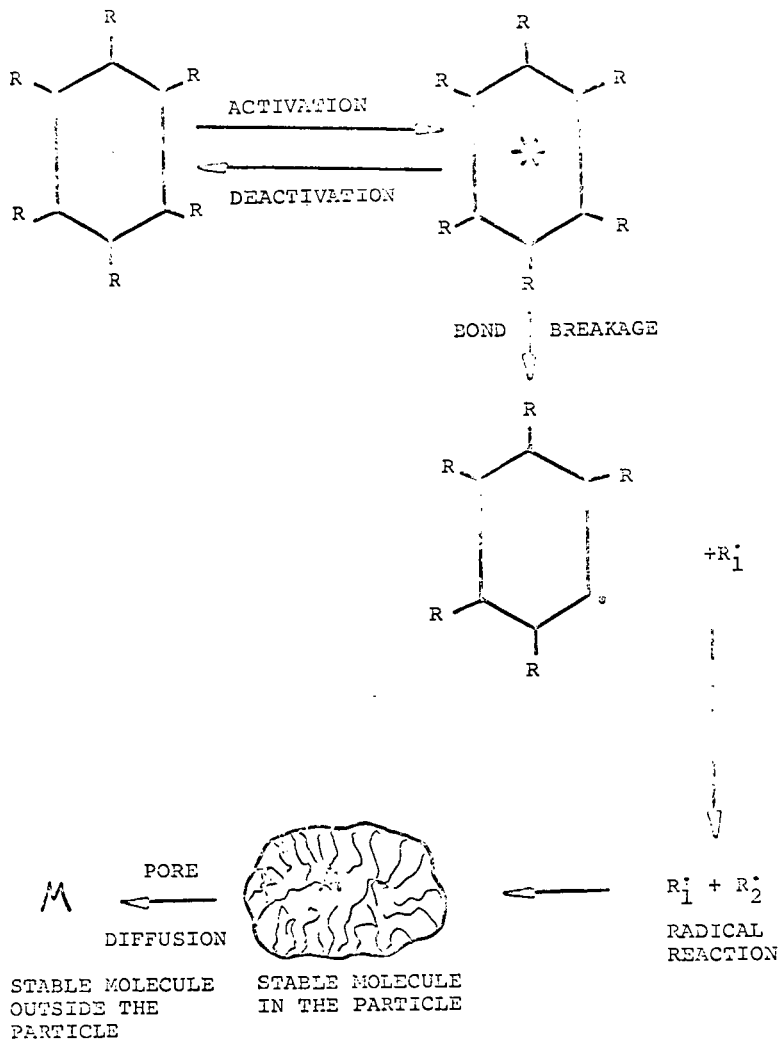


FIG. 1 MECHANISM OF COAL PYROLYSIS (JUENTGEN, VAN NEEK, [22])

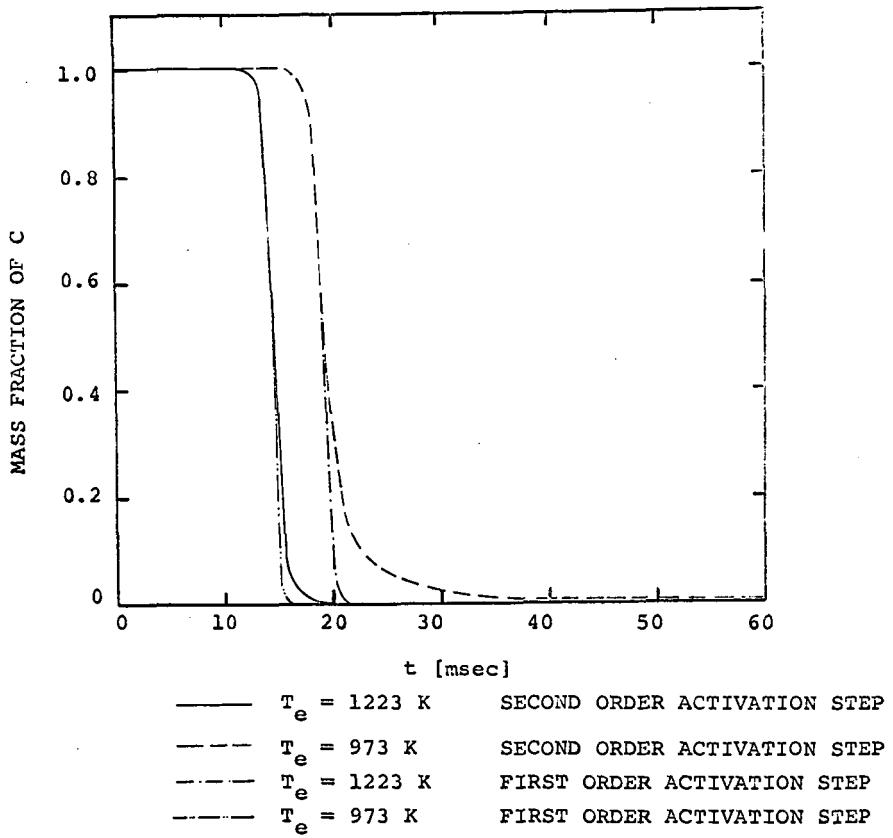


FIG. 2 INFLUENCE OF THE REACTION ORDER OF THE ACTIVATION STEP ON THE CONVERSION OF COAL TO ACTIVATED COAL.

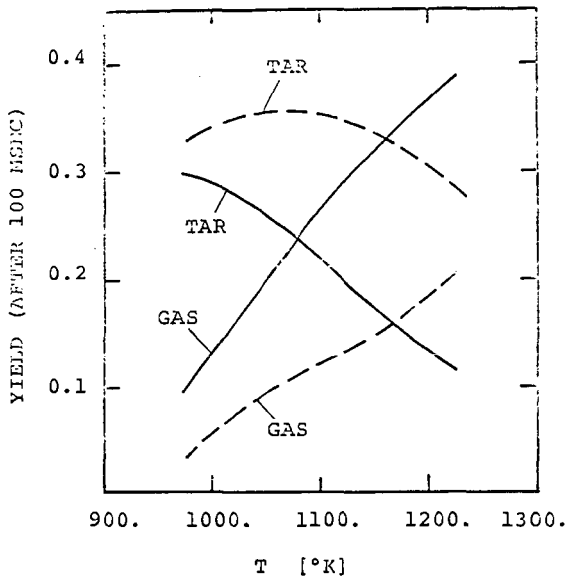


FIG. 3 VARIATION OF THE KINETIC VALUES OF REACTIONS 2 AND 3.

—————	$E_2 = 5. \text{ kcal/mole}$	$E_3 = 30. \text{ kcal/mole}$
-----	$E_2 = 10.7 \text{ kcal/mole}$	$E_3 = 40. \text{ kcal/mole}$

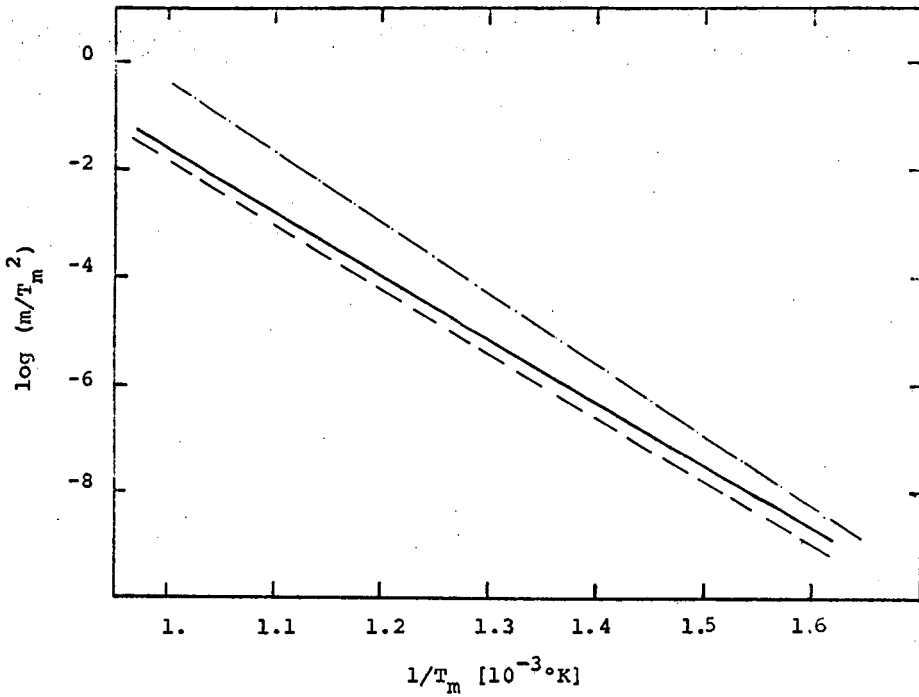


FIG. 4 INFLUENCE OF THE HEATING RATE m ON THE TEMPERATURE OF MAXIMUM GAS RELEASE T_m .

- THEORETICAL RESULTS
- EXPERIMENTAL RESULTS FOR CH_4 FORMATION [2]
- · - · - EXPERIMENTAL RESULTS FOR C_2H_6 FORMATION [2]

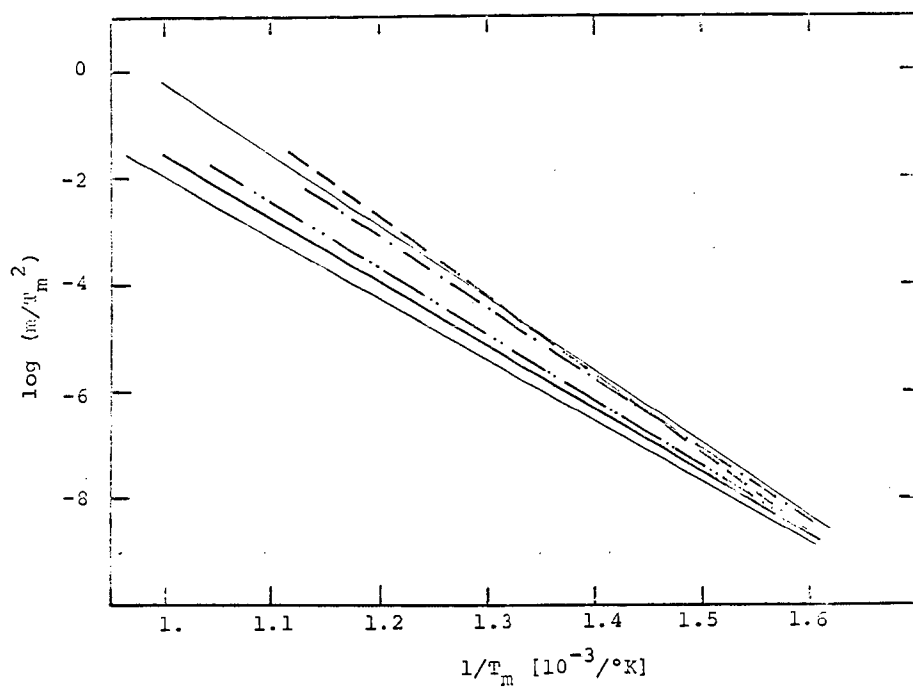


FIG. 5 INFLUENCE OF E_4 ON THE RELATION BETWEEN T_m AND m .

- $E_4 = 37$ kcal/mole
- · - · - $E_4 = 43.7$ kcal/mole
- $E_4 = 50$ kcal/mole
- $E_4 = 55$ kcal/mole
- Experimental results for CH_4 and C_2H_6 [2]

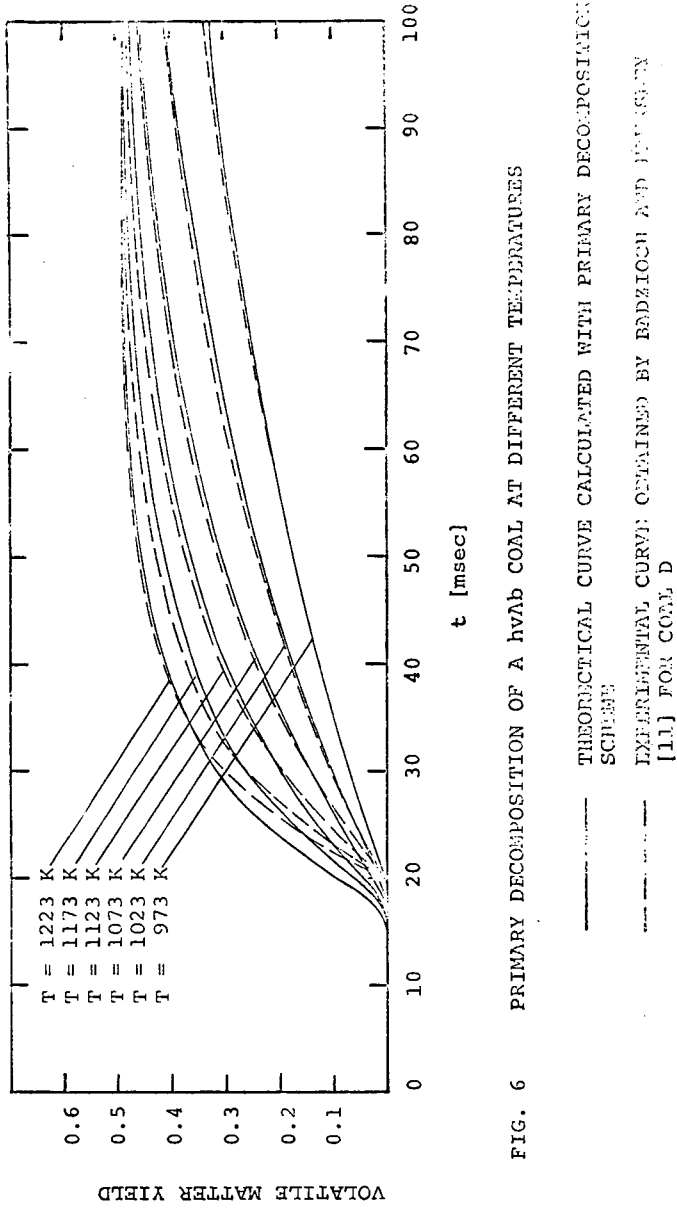


FIG. 6 PRIMARY DECOMPOSITION OF A hvab COAL AT DIFFERENT TEMPERATURES

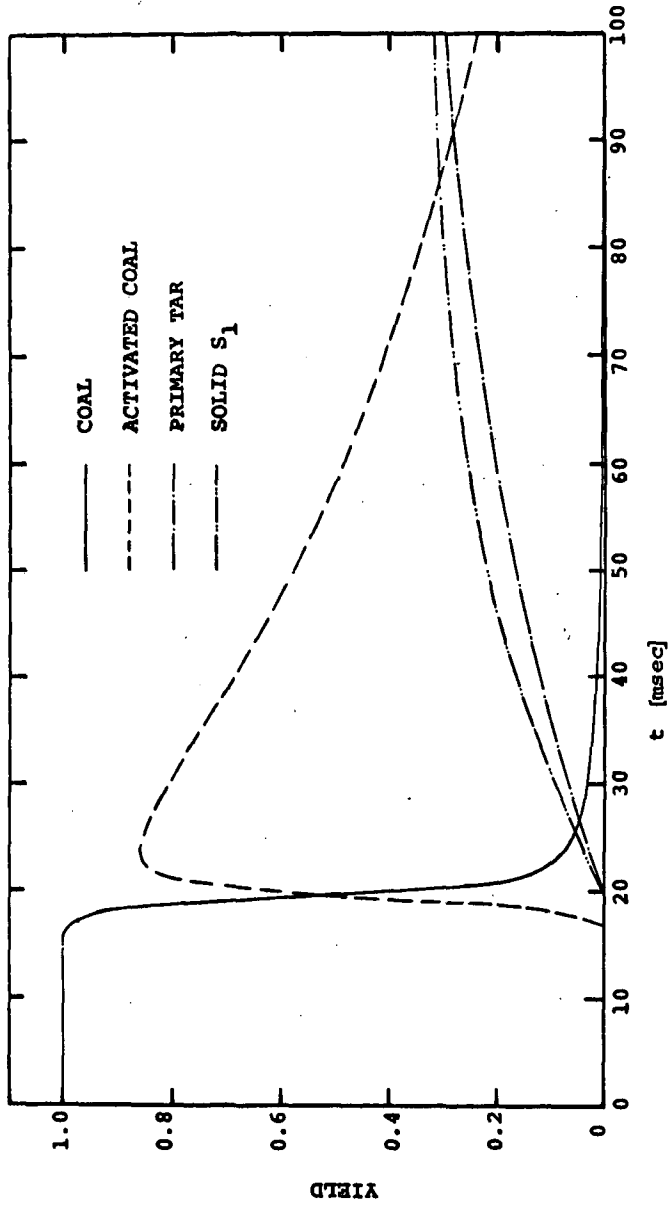


FIG. 7 PRIMARY DECOMPOSITION AT $T = 973^{\circ}\text{K}$ PRODUCT DISTRIBUTION

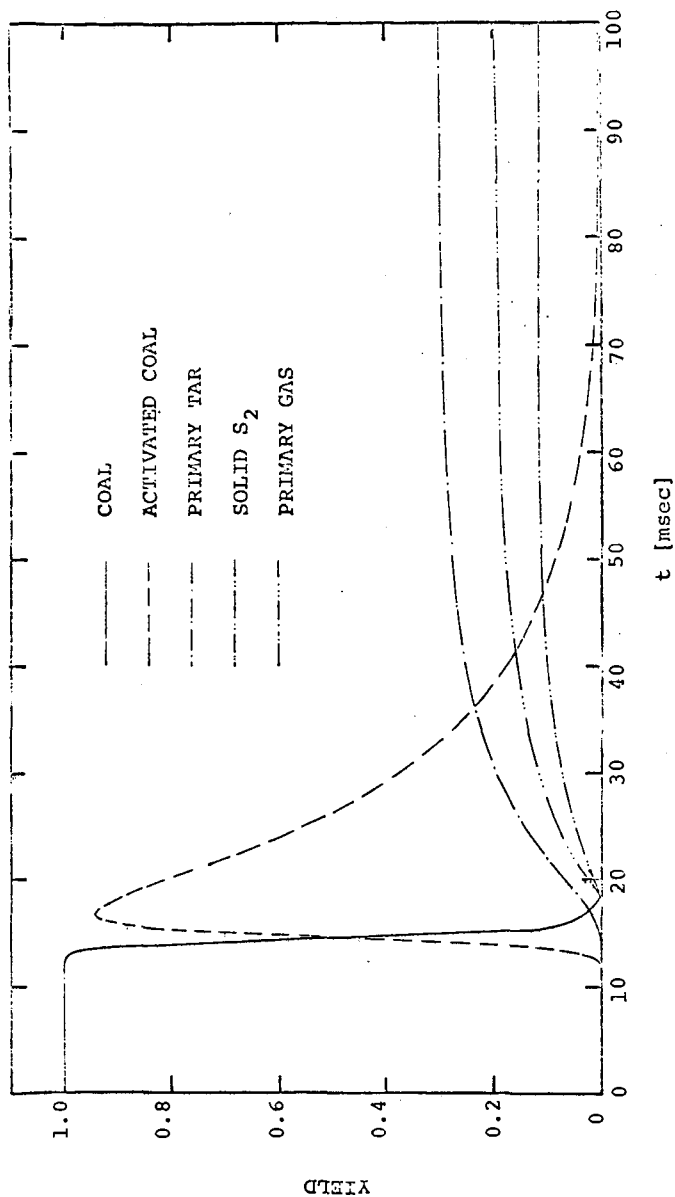


FIG. 8 PRIMARY DECOMPOSITION AT $T = 1223^{\circ}\text{K}$ PRODUCT DISTRIBUTION

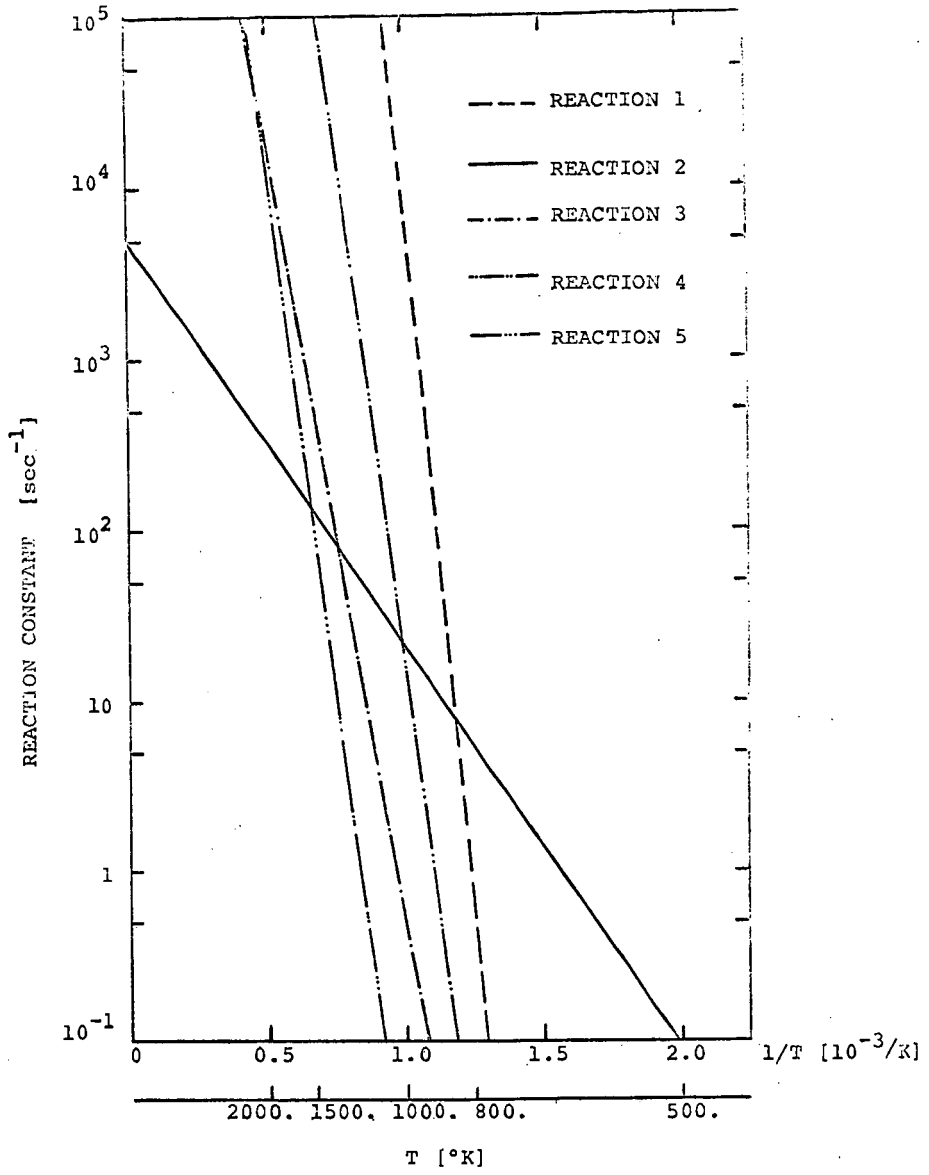


FIG. 9 REACTION CONSTANTS FOR THE PRIMARY DECOMPOSITION REACTIONS 1-5.